PB84-246248

Alternative Disinfection Processes

(U.S.) Municipal Environmental Research Lab.
Cincinnati, OH

Sep 84

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/D-84-221	2.
3. RECIPIENT'S ACCESSION NO. PB84 246248	
4. TITLE AND SUBTITLE Alternate Disinfection Practices	5. REPORT DATE September 1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Alan A. Stevens and James M. Symons	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Municipal Environmental Research Lab.-Cinti., OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268	10. PROGRAM ELEMENT NO. BNC1A 11. CONTRACT/GRANT NO. NA
12. SPONSORING AGENCY NAME AND ADDRESS Same as above	13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES

Project Officer: Alan A. Stevens - (513)684-7342

16. ABSTRACT

Trihalomethanes are formed during drinking water treatment when the free chlorine used as a disinfectant combines with trihalomethane precursors, mainly humic materials, present in the water. One approach to lowering trihalomethane concentrations in finished drinking water is by switching from free chlorination to an alternative disinfection process. The alternative processes vary widely in their tendencies to form byproducts other than trihalomethanes, the state of knowledge of their respective byproduct production, their disinfecting capabilities, and the engineering considerations associated with their application as a treatment process.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 44
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

PB84-246248

EPA-600/D-84-221
September 1984

ALTERNATIVE DISINFECTION PROCESSES

by

Alan A. Stevens
USEPA, Cincinnati, Ohio

and

James M. Symons
University of Houston
Houston, Texas

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

1. Introduction

Trihalomethanes are formed during drinking water treatment when the free chlorine used as a disinfectant combines with trihalomethane precursors present in the water (1,2). The four trihalomethanes most commonly found in finished drinking water are chloroform, bromodichloromethane, dibromochloromethane, and bromoform (3). A fifth, dichloroiodomethane is found much less frequently (4). A source of organic precursors that reacts with chlorine is aquatic humic materials found in virtually all drinking water sources, especially surface supplies (1,5). These humic materials include both humic- and fulvic acids that when present in high concentration, account for much of the color in those waters. Natural bromide and iodide are a source of the non-chlorine halogens (6).

The concentrations of trihalomethanes observed in water treatment and distribution are heavily dependent on reaction time, humic material concentration, pH, temperature, and to a smaller extent, chlorine dose and residual (5,7). Formation is strongly dependent on chlorine dose when the reaction is chlorine limited, but little change is usually seen in chloroform concentration once the demand requirement has been met and a reasonable residual maintained (4,8).

Bromide ion, even at very low concentrations relative to the applied chlorine, strongly influences the mixture of trihalomethanes formed. This occurs as a result of rapid oxidation of Br^- to HOBr followed by reaction of this active species with the organic precursor. The reaction of bromine with humic substances is much more rapid than that of chlorine resulting in both the disproportionate share of bromine-containing species and approaching a final trihalomethane concentration much earlier (usually minutes rather than hours or days) (4).

One approach (4) to controlling trihalomethane concentrations is the use of a disinfectant other than free chlorine that does not participate in these reactions. Several agents are possible alternatives to free chlorine for disinfection: chloramines (combined chlorine), chlorine dioxide, ozone, potassium permanganate, hydrogen peroxide, bromine chloride, bromine, iodine, ferrate ion, hydroxide ion (high pH), silver, and ultra-violet radiation. Of these, chloramines, chlorine dioxide, and ozone are the most commonly used as disinfectants in drinking water treatment practice today and have been studied in detail. The others are less significant in use for disinfection. Discussion in this chapter is weighted according to this use pattern.

2. General Considerations - Biocidal Activity

The primary reason for the use of disinfectants in drinking water is to ensure the destruction of pathogenic microorganisms during the treatment process, thereby preventing the transmission of waterborne disease. Secondarily, the presence of a disinfectant in the water distribution system helps to maintain the quality of water by preventing the growth of microorganisms.

2.1 Kinetics and Comparative Efficiencies (Free Chlorine, Chloramines, ClO_2 and Ozone)

Biocidal activity by chemical disinfectants has frequently been considered a kinetic process similar to a chemical reaction, the microorganism being considered as one of the substances involved in the reaction. The effectiveness or efficiency of biocidal agents is determined by the rate at which the reaction or killing of the microorganism population proceeds.

For example, data from the results of a number of experiments conducted using different disinfectants at various concentrations can be used to

construct plots of the type shown in Figure 11.1. As indicated, these results show the exposure times and concentrations of several disinfectants needed to produce a given level of inactivation of a given microorganism. Figure 11.1 is a composite of results obtained in one laboratory over a period of years using consistent experimental methods and microorganisms (8,9). The results show that chlorine dioxide at pH 7 and HOCl at pH 6 produce similar rates of inactivation of Escherichia coli. Hypochlorite ion was less effective, and monochloramine at pH 9 and dichloramine at pH 4.5 were even less so. From the data shown in Figure 11.1, the degree of difference in efficiency between the disinfectants should be calculated and expressed quantitatively. For example, HOCl at pH 6 is 35 times as effective as OCl at pH 10. A similar plot showing virucidal efficiency of these disinfectants of poliovirus 1 is shown in Figure 11.2 (9,10). Note that higher disinfectant concentrations and longer contact times, in general, are needed for inactivation of poliovirus 1 than for E. coli. The differences are less than 1 to 2 orders of magnitude, depending on the disinfectant used. Also, the difference in efficiency between HOCl at pH 6 and OCl^- at pH 10 is only about 4-fold, and the efficiency order of the two types of combined chlorine is reversed as compared to the E. coli data.

Studies from which similar curves can be prepared have not been performed using ozone as the disinfectant, primarily because ozone is such a powerful and unstable disinfectant that limitations on sampling times and ozone measurements make obtaining good experimental results difficult. In spite of this experimental difficulty, ozone is known to inactivate microorganisms rapidly.

2.1.1 Microorganism Effects on Comparative Efficiencies

As shown in Figures 11.1 and 11.2, neither the order of efficiency nor the degree of difference between the disinfectants is the same for E. coli as for poliovirus 1. Further evidence of such differences is shown in Table 11.1. This study examined the inactivation rates of six different enteroviruses by HOCl at pH 6 and by OCl^- at pH 10 (11). The results indicate that the degree of difference in disinfection efficiency of HOCl at pH 6 and of OCl^- at pH 10 ranged from 5-fold for Coxsackie A9 virus to 192-fold for ECHO 1 virus. Also note the occurrence of differences of 10-fold and 53-fold in the rates of inactivation of all other viruses by HOCl at pH 6 and OCl^- at pH 10.

TABLE 11.1. VIRUS INACTIVATION BY FREE RESIDUAL CHLORINE (11)

Virus strain	Minutes required for 99% inactivation at 5.0 ± 0.2°C (41 ± 0.4°F)		
	pH 6.0	pH 10.0	Ratio*
Coxsackie A9 (Griggs)	0.3	1.5	5
ECHO 1 (Farouk)	0.5	96.0	192
Polio 2 (Lansing)	1.2	64.0	53
ECHO 5 (Noyce)	1.3	27.0	21
Polio 1 (Mahoney)	2.1	21.0	10
Coxsackie B5 (Faulkner)	3.4	66.0	19

*Time required at pH 10.0/time required at pH 6.0.

2.1.2 Disinfectant Chemistry Effects on Comparative Efficiencies

Assessing the efficiencies of different free and combined chlorine species also is complicated by the nature of the chemical reactions that determine the chemical species present and the chemical equilibria established under various pH conditions. For instance, in the reaction

$HOCl \rightleftharpoons H^+ + OCl^-$ [Equation 1]

a rapidly achieved equilibrium exists that is drastically influenced by pH. At pH 10, however, approximately 0.5 percent of the free residual chlorine is still present as HOCl, and because it is a much more powerful biocide than OCl^-, its presence could substantially influence the biocidal activity observed.

Similarly, Equation 2 is reversible,

$HOCl + NH_3 \rightleftharpoons NH_2Cl + H_2O$ [Equation 2]

and a solution of 2 mg/L NH_2Cl is estimated to be 0.58 percent hydrolyzed (0.58 percent HOCl) at pH 7 and 25°C (77°F) (12). Because of the much higher biocidal efficiency of HOCl, its influence on the disinfection rate observed could be substantial and could explain the influence of pH on the biocidal efficiency of monochloramine.

Furthermore, the equation:

$H^+ + 2NH_2Cl \rightleftharpoons NH_4^+ + NHCl_2$ [Equation 3]

indicates that although mostly monochloramine is formed when excess ammonia is present at high pH (>8), addition of hydrogen ion (lowering pH) will cause formation of dichloramine, with the position of this equilibrium being determined by the pH of the treated water. Thus, with chlorine and chloramines, pure species are never present, and pH determines their identities. The influence of pH therefore cannot be experimentally separated from species effectiveness for disinfection.

Nevertheless, in the case of chlorine, disinfection efficiency does decline rapidly as the pH is increased from 7 to 9. The efficiency of chlorine dioxide also changes substantially over this pH range; but in contrast to chlorine, the effectiveness increases as the pH increases (9).

In this case, the change appears to be in microorganism sensitivity rather than in disinfectant species present, because unlike chlorine, chlorine dioxide does not quickly dissociate or disproportionate into different chemical species within this pH range. In earlier studies, a similar effect was shown with E. coli (i.e., more rapid inactivation at pH 8.5 than at lower pH by equivalent concentrations of chlorine dioxide) (13).

The pH of the water also affects ozone chemistry. At high pH values, ozone decay is accelerated, proceeding through hydroxyl radical intermediates; therefore, the pH of the water being treated may also influence ozone effectiveness.

Thus, the influence of many factors on disinfection make precise rankings of these three alternative disinfectants ozone, chlorine dioxide, and chloramines difficult. Nevertheless, chloramines are generally ranked as disinfectants that are weaker than free chlorine at all pH values. The National Research Council (NRC) Safe Drinking Water Committee rated chloramines moderate to low in relative disinfection ability and unsuitable as a primary drinking water disinfectant (14). In general, ozone and chlorine dioxide are ranked as strong disinfectants that are nearly equal to or better than free chlorine for destruction of pathogens.

Despite the generally weaker biocidal efficency of chloramines, the chlorine-ammonia treatment process has been used successfully for primary disinfection for years by a number of utilities. The chloramine formation as accomplished in these treatment plants differs significantly, however, from the procedures used in preparing chloramine for use in the laboratory chloramine disinfection studies described above. In experimental work, the chloramines are generally preformed and the microorganisms are added subsequently. In chlorine-ammonia treatment for primary disinfection, as practiced in the field, ammonia and chlorine are added to the water either simultaneously or in close succession.

Depending on pH, temperature, mixing efficiency, and the chlorine/ammonia ratio present, free chlorine may persist in practice, for several minutes and result in rapid inactivation of microorganisms during that time. Subsequently, chloramines will persist for long periods of time, continuing its disinfection action in waters that exhibit a strong chlorine demand that may rapidly deplete a free residual. Given sufficient contact time, the weaker disinfectants still provide an adequate microbiological quality.

Often a free chlorine residual is maintained for some period of time intentionally before ammonia is added, taking advantage of a rapid organism inactivation, followed by a stable chloramine residual in the distribution system. This usefulness of chloramines as an effective secondary disinfectant is recognized in the NRC report (14).

2.2. Comparative Efficiencies of Other Alternatives to Free Chlorine

Because of the lack of widespread use of the remaining disinfectant chemicals listed in Sec. 1 of this Chapter, detailed discussion of experimental results is beyond the scope of this chapter. The NRC Report (14) attempted to summarize the relative efficiencies shown in Table 11.2 for demand free systems. Free chlorine is shown for comparison purposes. Thus, some alternatives listed in Table 11.2 have disinfectant properties that are as useful as free chlorine while others are clearly not as good or have unknown comparative worth. Considerations other than efficacy in laboratory situations, such as engineering or cost considerations, ultimately determine their reliable usefulness. Bromine chloride was not included in Table A but is essentially an alternate method for introducing bromine as the disinfection agent (14).

TABLE 11.2. SUMMARY OF EFFICACIES OF LESS COMMON ALTERNATE DISINFECTANTS BIOCIDAL ACTIVITY BY ORGANISM CLASS (14)

Agent	Bacteria	Virus	Cysts
Free chlorine* (HOCl)	Excellent	Excellent	Moderate
Permanganate	Questionable	-	-
Hydrogen Peroxide	Questionable	Questionable	-
Bromine	Excellent	Excellent	Good
Iodine (as I_2)	Excellent	Good	Good
Iodine as HOI)	Excellent	Excellent	Low
Ferrate	Moderate	Good	-
Elevated pH (>12)	Good	Good	-
Silver	Low	-	Low
UV Radiation	Good	Good	-

*for comparison to others
-means unknown

2.3 Extrapolation from Laboratory Studies to Field Situations

Although information derived from laboratory studies is very useful in assessing the relative biocidal efficiency of disinfectants, other factors are important in the application of this information to actual drinking water treatment in the field. In water treatment, pure cultures of organisms are not present as clean suspensions in a medium free of extraneous materials that might react with the disinfectant used, thereby destroying or altering its biocidal capability. Rather, in the field, a variety of microorganisms are present in their natural state, suspended in a medium containing a variety of other solid and dissolved materials, some of which can have pronounced effects on disinfectant concentration and activity. Because of these factors, disinfection in the field does not behave as a constant rate process as it does in laboratory studies. These effects change the shape of the decay curves and perhaps even the order of overall effectiveness observed. Additionally, particulate matter (turbidity) is thought to shield both

viruses (15) and bacteria (16) from the disinfection process. Indeed, supposed protection of microorganisms by their association with particulate matter has been the major consideration in establishing a turbidity limit for drinking water. Thus, site specific water quality considerations are very important in determining the most appropriate disinfectant to accomplish the microbiologocal quality goals.

3. Formation of Trihalomethanes by Alternatives to Free Chlorine

One of several alternatives to prevent formation of trihalomethanes from chlorination of drinking water is to use a disinfectant that does not produce this undesirable side reaction product. Below, the most commonly considered alternatives are discussed with respect to their tendency to form trihalomethanes.

3.1 Chloramines

The reaction of free chlorine with ammonia to form mono- and dichloramine have been discussed above (Chapt. 11, Sec. 2.1.2). In addition to eq. 2 and 3, other reactions are important in the so called breakpoint chlorination process. Sequential reactions occur to form monochloramine, dichloramine, and nitrogen trichloride. Oxidation occurs in the process when sufficient chlorine excess is present to remove the ammonia as nitrogen gas and chlorine residual is reduced to chloride (eq. 4).

$$2NHCl_2 + H_2O \longrightarrow N_2 + HOCl + 3H^+ + 3\ Cl^- \qquad \text{(Equation 4)}$$

This is somewhat simplified, and the end result is heavily dependent on pH. The general process is graphically depicted in Figure 11.3. The breakpoint curve has been divided into three regions that are important to understand if the influence of ammonia/chlorine on the formation of trihalomethanes when "chloramines" are used as a disinfectant is to be understood.

3.1.1 Region A

In Region A, Fig. 11.3 the reactions of chlorine and ammonia to form combined chlorine are very fast relative to trihalomethane formation; very little free chlorine is present, and when chlormaines are preformed, or ammonia is present in stoichiometric excess, trihalomethanes do not form to a significant degree (Fig. 11.4) (7).

These data show little development of chloroform during the 70 hours of exposure when combined chlorine was the disinfectant. In contrast, much higher concentrations of chloroform were formed in the presence of a free chlorine residual.

Symons, et al. (4) document twelve instances when chloramines were used or when ammonia was added after a period of free chlorination to form chloramines at treatment plants. These data show lower resulting trihalomethane concentrations when compared with situations in which free chlorine was the disinfectant. Some utilities included were St. Louis County (Missouri), Beaver Falls, PA; Jefferson Parish, LA; Huron, SD; Casitas, CA; and Stuttgardt, West Germany; indicating that over a wide geographic area, the conclusions drawn from Fig. 11.4 appeared valid. More recently, many utilities have changed to combined chlorine to meet the requirements of the trihalomethane regulation.

3.1.2 Region B

In Region B, Fig. 11.3, the oxidation reactions, such as that of equation 4, are occurring in the presence of excess chlorine. The oxidation reactions are much slower than the initial chloramine formation reactions, and, thus, free chlorine can persist for many minutes, although probably less than an hour (17). this will allow significant trihalomethane formation during that

time after adding the chlorine. This phenomenon has been observed at at least one utility where breakpoint chlorination has been historically necessary to remove ammonia from the source water (18). Thus, trihalomethane control is not complete when chloramine treatment is attempted in Region B.

3.1.3. Region C

After breakpoint (Fig. 11.3) mainly free chlorine exists and no trihalomethane control is expected. Chlorination into Region C is usually a strategy to remove ammonia by oxidation, counter to the intent of trihalomethane control by chloramine treatment.

3.1.4. Bromide Problems with Chloramine/Breakpoint

Lange and Kawczynski, in their efforts to control trihalomethane concentrations at the Contra Costa County Water District, experimented with the use of chloramines (19). They conducted jar tests arranged to resemble treatment at the water plant with source water chlorination, ammonia being added to the chlorinated water at a weight ratio of 3/1 (NH_3/Cl_2). The data (Table 11.3) show that the addition of ammonia did arrest the formation of trihalomethanes. Because the high bromide concentration caused a rapid formation of bromine-containing trihalomethanes, however, very little time could be allowed to elapse between the addition of chlorine and ammonia if significant reductions in trihalomethane concentrations were to be achieved. The California State Department of Health required a free chlorine residual be maintained for a minimum of 10 minutes before the addition of ammonia. Other Primacy States may have similar requirements. Thus, utilities with source waters having a high bromide content within these Primacy juridictions may experience difficulty controlling trihalomethanes with chlorine-ammonia treatment. Recent studies have shown that the free chlorine concentration and contact time may be reduced considerably with adequate disinfection, minimizing trihalomethane formation if mixing intensity is sufficiently great (20).

TABLE 11.3. RESULTS OF CHLORAMINE STUDIES AT CONTRA COSTA, CA, SEPTEMBER 1977 (19)

Cl_2 contact time before adding NH_3		Trihalomethanes, ug/L				
hr	pH	$CHCl_3$	$CHBrCl_2$	CHB_2Cl	$CHBr_3$	Total ug/L
0	7.0	3	2	1	<1	6
0.5	7.0	15	16	39	50	120
1.0	7.0	7	18	45	55	125
1.5	7.0	8	20	51	60	139
4.0	7.0	9	26	58	50	143
Control treatment sample (excess Cl_2)	8.2	5	18	84	189	296

Thus, the presence of bromide in source waters lessens the effectivenss of trihalomethane control by chloramine treatment even with Region A of the breakpoint curve.

3.2 Chlorine Dioxide

In 1976 Miltner (21) completed work that demonstrated that pure chlorine dioxide would not cause formation of trihalomethanes. A study was conducted in which a humic acid solution (5 mg/L) was dosed with 8 mg/L chlorine dioxide. After 48 hours of contact time, 1.7 ug/L of chloroform was formed (Figure 11.5), but no other trihalomethane species occurred. For comparison, a similar humic acid solution was dosed with 8 mg/L of free chlorine. In the same time period, 108 ug/L of chloroform (figure 11.5) and 1.5 ug/L of bromodichloromethane were formed - about 110 ug/L TTHM. This study indicates that chlorine dioxide does not produce trihalomethanes from precursor materials that will react with free chlorine to produce trihalomethanes. Other work with Ohio River water confirmed that this general conclusion applies to the natural aqueous medium.

During normal continuous flow operation, chlorine dioxide is usually generated under conditions that result in mixtures of free chlorine and chlorine dioxide (see Sec. 5.1, this Chapter). Although the presence of chlorine suggests that trihalomethanes would be formed under these circumstances, for reasons not yet understood, chlorine dioxide alters certain trihalomethane precursors so that the yield of trihalomethanes is reduced when free chlorine reacts with them. Trihalomethane concentrations tend to be inversely related to the chlorine dioxide/free chlorine ratio (4). Concentrations of trihalomethanes, therefore, can be kept low if the excess free chlorine used to produce chlorine dioxide is carefully controlled. Use of chlorine dioxide as a pretreatment oxidant is discussed in Chapter 10.

Symons et al. (4) document several cases where chlorine dioxide has been used successfully, either alone or in conjunction with chlorine to successfully lower trihalomethane concentrations at both at the pilot- and full scale.

3.3 Ozone

Trihalomethane formation under practical drinking water treatment conditions, especially with waters low in bromide contant, appears not to be a problem (4). The issue of formation of HOBr from bromide and, thus, subsequent bromoform formation is controversial. The subject was recently reviewed by Cooper (22). This review indicates that competing reactions involving ozone, precursors, bromide, bromate, and $HOBr/OBr^-$, depend on the concentrations of each and on pH. At normal water treatment pH values, ozone doses between those necessary to oxidize humics (low, to meet demand) and those necessary to oxidize $HOBr/OBr^-$ to BrO_3^- (high) will result in bromoform production in waters relatively high in bromide.

3.4 Bromine, Bromine Chloride

Hypobromous acid is the expected active species upon hydrolysis of either applied Br_2 or BrCl, in both cases, bromoform would be expected to form. Symons' (4) review describes an EPA study that verified these expectations. In this study, when free chromine was used as a disinfectant, the primary trihalomethane was chloroform, but when bromine chloride was used as a disinfectant, nearly all of the trihalomethane content appeared as bromoform (Table 11.4).

TABLE 11.4. TRIHALOMETHANE FORMATION IN TREATED WATER DISINFECTED WITH CHLORINE AND BROMINE CHLORIDE (4)

Reaction time, hr	Trihalomethanes formed with Cl_2, ug/L				Trihalomethanes formed with BrCl, ug/L			
	$CHCl_3$,	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	$CHCL_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$
6	44	16	3.4	0.2	0.3	0.1	1.7	149
24	85	23	4.5	1.3	0.4	0.1	2.0	177
48	106	28	5.2	0.5	0.5	0.1	2.7	194
72	116	30	5.8	0.6	0.6	0.2	3.2	209
96	118	41	5.9	0.5	0.5	0.1	3.4	209

Furthermore, when summed, the TTHM concentration would be much higher for the BrCl-treated water indicating that use of these agents as substitutes for chlorine for trihalomethane control would be counterproductive.

3.5 Iodine

The formation of trihalomethanes during iodination was studied by Rickabaugh and Kinman (23). Their findings showed that none of the regulated trihalomethanes (24) were formed when iodine as used as the disinfectant.

Some iodoform may have been formed, but analysis did not include this compound.

Indeed, iodination to form iodoform is the basis for the classis haloform test for methyl ketones. Iodomethanes form during chlorination of waters containing iodide ion, presumably through an iodine intermediate, in a manner analogous to bromomethane species formation from chlorination of waters containing bromide (6).

3.6 Trihalomethane Formation from Other Alternative Disinfectants

No evidence could be found by the authors to indicate that permanganate, hydrogen peroxide, ferrate, silver, high pH, or ultraviolet radiation would themselves cause formation of trihalomethanes in natural waters.

4. Formation of Byproducts Other than Trihalomethanes

When any disinfectants are used in water treatment, byproducts other than trihalomethanes may be found. Most is known about the byproducts of the reactions of chlorine, chlorine dioxide, ozone, and chloramines because these commonly used oxidants have been subjected to the most intense study. Little can be found in the literature about byproducts from the other disinfectants addressed in this chapter; thus, the organic byproducts of reactions of only chlorine, chlorine dioxide, O_3, and chloramines are reviewed in a relatively detailed way, and separately, the inorganic end products from all of the disinfectants discussed in this Chapter are summarized.

4.1 Organic Byproducts

4.1.1 Specific Compounds from Chlorine

Nonpolar compounds other than trihalomethanes that were either not detectable in the source water or were present in lower concentrations have

been detected in finished water at ng/L to ug/L concentrations. The sources of most of these are poorly understood. At least 19 nontrihalomethane, halogenated, volatile compounds were found by Rook (25) in the Rotterdam Storage Reservoir. Stieglitz et al. found additional compounds formed at low concentrations in a Rhine River bank filtrate sample upon chlorination (26). Rook speculated on a possible pathway to explain the formation of some of the observed byproducts as related to his proposed mechanism for trihalomethane formation from m-dihydroxyphenyl moieties. Stieglitz suggested no mechanism. Coleman et al. reported the co-presence of chloropicrin, chlorobenzene, a chlorotoluene isomer, and a chloroxylene isomer as well as their repective logical precursors (nitromethane, benzene, toluene, and m-xylene) in finished chlorinated tap water (27). With the exception of benzene, all of the above precursors were shown to react with free chlorine to form the expected products.

In other studies reported by Symons et al. (4) haloacetonitriles were observed in a finished tap water. Concentrations of acetonitrile in the mg/L range could not be made to react with free chlorine under realistic reaction conditions to form detectable chlorinated derivatives. But Trehy showed that dichloro-, bromochloro-, and dibromoactontrile were formed upon low pH chlorination of a south Florida drinking water source (28). At high pH, such as in lime softening systems these byproducts are less of a problem. Suffet et al. has found 1,1,1-trichloroacetone in two tap waters, but not in the respective source waters (29). Later work at Manchester, NH has shown the formation of dichloro- and 1,1,1-trichloroacetone upon chlorination (4). Dichloro- and trichloroacetic acids are now thought to be major products of chlorination of humic materials, under some conditions exceeding

the concentrations of trihalomethanes (30). At this writing, literally hundreds of discrete minor byproducts of treatment of humic materials with chlorine have been detected, mostly aromatic and aliphatic acids, some containing halogen (31-33). The majority of these, determined to be unique by their mass spectra, have not been fully characterized or identified.

4.1.2 Specific Compounds from Chlorine Dioxide

Although chlorine dioxide does not react to produce trihalomethanes, chlorine dioxide does react with organic material during water treatment and, like chlorine, is therefore likely to produce other organic byproducts. Chlorine dioxide reacts with natural humic acids, reducing the concentration of color in drinking water supplies (34). Similarly, large quantities of ClO_2 are used for bleaching operations in the pulp and paper industry. Much work on the byproducts of this process has been preformed and formed the basis for a review of the subject in a way pertinent to drinking water applications by Stevens (35). Briefly, the reivew described chlorinated and nonchlorinated derivatives (including acids, epoxides, quinones, aldehydes, disulfides, and sulfonic acids) that are products of reactions carried out under conditions somewhat different from those experienced at water treatment plants.

As a follow-up to this review, some studies have been conducted to explore the formation of byproducts under conditions more closely related to drinking water treatment conditions. Semiquantitative results of one study have been described where C_2 through C_8 aldehydes were noted to increase in concentration after treatment of a natural water with chlorine dioxide (35). In that work, no other dramatic differences were observed

between treated and untreated samples with regard to compounds amendable to the type of gas chromatographic analysis used. Other studies have since shown that many of the same aromatic and aliphatic acidic compounds seen upon chlorine treatment are also seen after ClO_2 treatment of natural humic materials (36).

4.1.3 Specific Compounds from Chloramines

The potential for formation of organic byproducts as a result of disinfection with chloramines is not as obvious as with chlorine dioxide. Chloramines are weaker disinfectants (less reactive with cells) compared to chlorine and chlorine dioxide, and waters generally exhibit a much lower disinfectant demand when chloramines are used. Because chloramines do hydrolyze to form traces of free chlorine, some reaction products of this oxidant might be expected, but at much lower concentrations in a given time than when free chlorination is practiced. Except for chlorine exchange reactions with primary and secondary amines present in treated waters, information regarding specific byproduct formation from chloramines under drinking water treatment conditions is virtually absent from the literature (14).

4.1.4 Specific Compounds from Ozone

Ozone is a highly reactive oxidant that might be expected to produce oxidation products of organic materials found in water supplies. Unlike the oxidants chlorine, chlorine dioxide, and chloramines, however, ozone would not be expected to produce chlorinated byproducts.

Although much is known about ozone reactions in other media, surprisingly little information exists about the action of ozone as an oxidant of organic compounds in aqueous solution. This lack of data exists even

though ozone has been in widespread use for decades as a water and wastewater disinfectant. The reviewed data suggest that oxygenated products such as ketones, aldehydes, and acids are most likely formed from alcohols and olefinic double-bond and aromatic ring cleavage (14).

Of the few studies performed in connection with drinking water treatment, a study by Schalekamp was revealing concerning byproduct formation (37). Schalekamp analyzed water before and after an ozone treatment step at various ozone doses. He found that the concentration of total C_6-C_{14} aldehydes rose by a factor of more than 10 as the ozone dose increased from 0 to 5 mg/L. Absolute concentrations were low, however, usually a few hundred nanograms per liter after ozonation and always less than 1 ug/L, depending on the aldehyde.

Sievers et al. also found the same aldehydes and reported some apparent hydrocarbon formation upon ozonation of the effluent from a secondary waste treatment plant in Estes Park, CO (38).

4.2 Inorganic End Products

The above discussion of byproducts ignores the possible problems surrounding the inorganic end products of chemical reduction of the oxidant disinfectant. A brief summary of these products is presented in Table 11.5. Most of the end products are natural constituents of the water matrix, and at the low concentrations normally applied, they blend into insignificance. Two major exceptions to this maybe the end products from ClO_2 and iodine. The USEPA has issued a recommendation limiting total oxidant residuals from ClO_2 (ClO_2, ClO_2^-, ClO_3^-) to 1 mg/L (39), and the possibility of adverse health effects of increased intake of iodine to susceptible individuals has been raised (14). Ferrate and permanganate produce end products that are usually easily removed in the treatment process.

TABLE 11.5. SUMMARY OF INORGANIC END PRODUCTS FROM USE OF DISINFECTANTS

Agents	End Product	End Product Significance
Cl_2, $HOCl/OCl^-$	Cl^-	Insignificant
Chloramines	persistent residual	Effects under study
ClO_2	ClO_2^-, ClO_3^-, Cl^-	Recommend 1 mg/L limit on ClO_2, + ClO_2^- + ClO_3^- on health effect basis
O_3	O_2, OH^-, H_2O	Insignificant
$KMnO_4$	MnO_2	Precipitates in treatment
H_2O_2	O_2, OH^-, H_2O	Insignificant
Br_2, BrCl, $HOBr/OBr^-$	Br^-	Insignificant
I_2, HOI/OI^-	I^-	Large iodine intake discouraged
FeO_4^{2-}	Ferric oxides/hydroxides	Precipitate in treatment
Elevated pH	H_2O	-
Ag/Ag^+	Residual/solids	-
UV	None	-

4.3 Organic Halogen

One approach to characterizing and quantifying byproduct formation from the disinfectants that contain halogen is to measure Total Organic Halogen (TOX) which can be done by use of an activated carbon adsorption-pyrolysis technique (40). This analytical technology has been applied to solutions of a soil humic acid that was treated separately with each of the three disinfectants: free chlorine, combined chlorine (chloramines), and chlorine dioxide. Time, temperature, pH, disinfectant dose, and organic substrate concentrations were varied. Selected examples of the results obtained are presented in Figures 11.6 and 11.7 (41).

The bar graphs in Figures 11.6 and 11.7 represent Non-Purgeable Organic Halogen (NPOX) above the zero line and Purgeable Organic Halogen (POX), measured as trihalomethanes (in this case exclusively $CHCl_3$), below the zero line. The full length of a bar, therefore, represents Total Organic Halogen (TOX). Arranged in this manner, the concentration of TOX in solution at 20°C (68°F) can be seen to be mostly composed of NPOX at pH values of 5 and 7, while at pH 11 the amount of trihalomethanes present is the greater, Fig. 11.7. The ratio of NPOX to trihalomethanes is shown to diminish with increasing pH, which occurs because increasing pH favors an increase in trihalomethane formation while at the same time promoting a drastic decrease in NPOX concentration.

The effect on organic halide formation of increasing the dose of chlorine from 8.1 mg/L to 20 mg/L at 20°C (68°F) is also demonstrated in Figure 11.6. Compared with the low dose, TOX is increased by 29, 36 and 27% at pH values near 5, 7 and 11, respectively, at the higher dose. This is caused almost entirely to an increase in NPOX formation.

Figure 11.6 also reveals a relatively rapid formation of NPOX within the first two hours after dosing with chlorine when compared to THM formation. All of these results of chlorination are typical of those reported for humic materials from other sources by Fleischacker and Randke (42).

Figure 11.7 compares the NPOX and trihalomethane formation at 20°C (68°F) at 3 different pH levels for each of the three disinfectants, chlorine, chloramines and chlorine dioxide. NPOX formation is reduced by 85% when comparing the use of chloramine as the disinfectant to chlorine and was even much lower when chlorine dioxide is used. Trihalomethane formation is reduced by greater than 95% when chloramines were used, and no trihalomethanes were detected when chlorine dioxide was used. Unlike with chlorine, which increases the formation of trihalomethanes with increasing pH, the use of chloramines and chlorine dioxide as disinfectants results in a decrease in the formation of all organic halides (including THMs) with increasing pH. NPOX formation with chlorine dioxide was rapid with no difference observed between 2 hr and 144 hr sample concentrations.

Similarly, two studies described by Symons et al (4) compared the formation of organic halogen when four different disinfectants were used to treat a natural surface water. In these experiments, Ohio River water that had been coagulated, settled, and filtered in a pilot plant was disinfected with free chlorine, chloramines, chlorine dioxide, and ozone. For this experiment, these data show that organic halogen is formed by the action of these disinfectants in the following order of yield (Table 11.6):

free chlorine > chloramines > chlorine dioxide > ozone

TABLE 11.6. FORMATION OF ORGANIC HALOGEN (OX) IN OHIO RIVER WATER TREATED WITH VARIOUS DISINFECTANTS (4)

(ug/L as Cl^-)

	Free Chlorine	Chloramines	Chlorine Dioxide	Ozone	Control (No Disinfectant)
Test 1	194 (2.5 mg/L)*	101 (2.0 mg/L)	61 (3.0 mg/L)	9 (3.0 mg/L)	17
Test 2	53 (3.3 mg/L)	26 (0.8 mg/L)	17 (2.4 mg/L)	11 (1.0 mg/L)	13

*Disinfectant dose is indicated in parentheses.

These tests confirm that the trends seen in the humic acid studies are applicable to natural waters as well.

Data from eight utilities to demonstrate the variability that may be caused by a number of the factors described above are presented in Table 11.7. The significance of the organic halogen measurement as an indicator of water quality has not been determined; thus, the usefulness of this approach to extimating the significance of byproduct formation is not yet known.

TABLE 11.7. ORGANIC HALOGEN (OX) IN FINISHED WATERS (4)

Utility	Nonpurgeable OX (NPOX) concentration, ug/L as Cl^-	Purgeable OX (POX) (mostly TTHM) ug/L as Cl^-	NPOX/POX Ratio
A	17	9.8	1.7
B	NF†	NF	-
C	52	64	08
D	36	31	1.2
E	165	180	0.9
F	136	114	1.2
G	66	133	0.5
H	98	27	3.6

† NF = none found

5.1 Application of Disinfectants

Engineering and other practical considerations of applying disinfectants is a subject area of rather large scope and has been the subject of a number of reviews (12, 14, 43). For this Chapter, discussion is limited to a brief overview of several common considerations for choice.

5.1.1 Chlorine

Since the beginning of this century, both liquid chlorine and dry forms (hypochorlites) have been used for drinking water chlorination in this country. During this time, the off-site manufacture and on-site feeding of these chemicals has become commonplace technology. Although good safety practices are required to handle these chemicals, chlorine is a good disinfectant, and a disinfectant residual can be maintained.

5.1.2 Chloramines

Chloramines can either be created by chlorination of ammonia present naturally in the water or ammonia that is added artifically. If ammonia is present in the source water, simply adding chlorine as noted previously, will produce chloramines. If no ammonia is present, feeders are available that will add any one of a variety of ammonia containing chemicals to the water. The ammonia can be added either before or after the chlorine, depending on the optimum arrangement at a given site. Although chloramines must be created on-site, they do produce a disinfectant residual and are widely used.

5.1.3 Ozone

Ozone must be produced on-site. This is accomplished by use of an ozonator. The ozonator is a device within which a stream of clean dry air or oxygen passes through an electrical discharge. On-site power requirements are a major consideration, about 13 to 22 kWh/kg of ozone generated from air and

approximately half that when oxygen is used. Compressors and dryers may increase overall power requirements by 20% to 50%. Other factors affecting efficiency of ozone production are the rate of gas flow, applied voltage, and the temperature of the gas. Approximately twice the percent of ozone by weight is obtained if oxygen, rather than air, is used as the feed stream. Heat produced during the process is a major problem and cooling must be provided.

The gas stream containing ozone is fed into the water to effect the transfer of ozone from the gas phase into the water. The usual methods are to inject the ozone gas stream through an orifice at the bottom of a co- or countercurrent contact chamber or to aspirate the gas into a contact chamber where it is mixed with the water mechanically.

The chief disadvantages to the use of ozone are the relatively complex generating equipment that must be operated on site, its poor solubility in water, its short half life, and, thus, the lack of residual. In practice, however, these problems have been successfully overcome, and ozone is widely used in Europe.

5.1.4 Chlorine Dioxide

The preparation and distribution of chlorine dioxide in bulk is not practical. Therefore, it too is generated and used on-site. Sodium chlorate or sodium chorite may be used to generate chlorine dioxide. The method of production will depend upon the amount of chlorine dioxide that is required. Compared to some industrial applications, use at a drinking water treatment plant is small, and sodium chlorite is the chemical of choice.

Chlorine dioxide can be prepared from the reaction of chlorine with sodium chlorite through the following:

$$Cl_2 + H_2O \rightarrow HOCl + HCl \qquad \text{(Equation 5)}$$

$$HOCl + HCl + 2NaClO_2 \rightarrow 2ClO_2 + 2NaCl + H_2O \qquad \text{(Equation 6)}$$

The theoretical weight ratio of sodium chlorite to chlorine is 1:0.39. With commericial grade sodium chlorite (80%), the weight ratio is 1:0.30. In practice, a chlorite to chlorine ratio of 1:1 is recommended. The excess chlorine lowers the pH, thereby increasing the reaction rate and optimizing the yield of chlorine dioxide.

Chlorine dioxide also may be prepared from sodium hypochlorite and sodium chlorite. The sodium hypochlorite is acidified to yield hypochlorous acid and the chlorine dioxide is generated according to Equation 6. Each of the methods produces a solution containing both chlorine and chlorine dioxide. Chlorine-free chlorine dioxide may be prepared by the addition of a strong acid, such as sulfuric acid or hydrochloric acid, to sodium chlorite.

Although chlorine dioxide must be generated on-site, the equipment is relatively simple, and a disinfectant residual is produced. Care must be taken in handling and storage of the sodium chlorite as it is unstable. Chlorine dioxide is widely used in Europe.

5.1.5 Others

The more common method of adding iodine to a municipal water supply produces the required concentration of iodine by passing water through a bed of crystalline iodine called a saturator. This has been used in many small, semipublic and private home water systems. Because the maximum concentration is limited by solubility to 200-300 mg/L at the ambient temperatures that are expected for drinking water, some physical complications would accompany the introduction of this method into the large waterworks system in view of the large saturation bed required. Another method

is to employ nonhazardous solvents and solubilizing agents such as ethyl alcohol or aqueous potassium iodide to overcome the low concentration of aqueous iodine stock for solution feeders. A disinfectant residual is produced.

Some difficulties that are encountered when handling liquid bromine and its corrosive nature have encouraged the use of bromine chloride as a technique for introduing bromine into water. Like chlorine, bromine chloride is produced off-site and shipped as the dry liquid in steel containers. Liquid bromine chloride is removed from cylinders under moderate pressure, then vaporized, and the gas is metered in equipment that is similar to that used for chlorine. Some special materials must be used in the gas feeders because bromine chloride is more reactive than chlorine with polyvinyl-chloride plastics. A disinfectant residual is produced.

High pH values in water are usually obtained by addition of either calcium hydroxide or sodium hydroxide. Calcium hydroxide is most often prepared by reaction of calcium oxide with water at the plant. All three chemicals may be easily obtained and none are particuarly dangerous to store, handle, or feed.

Off-site commercially produced hydrogen peroxide is available in aqueous solution, usually ranging from 30% to 90%. A concentrated solution would be diluted and then applied with a chemical metering pump. Little experience exists with this in water plant operations partly because hydrogen peroxide is not presently considered to be a disinfectant in the water industry. Fire or explosion hazards exist with the concentrated solutions, requiring care in handling.

Potassium permanganate is readily available in crystalline form. In waterworks, a dilute solution of a few percent is usually prepared and

applied with a chemical metering pump. Permanganate may also be added by using conventional dry-feed equipment. Although not normally used as a disinfectant, potassium permanganate is widely used in water treatment practice for controlling taste and odor.

A wide variety of metallic ferrate salts have been prepared. However, only a few of the preparations yield ferrates of sufficient purity and stability for use in the treatment of water. In contrast to permanganate, ferrates are not typically presently available in large bulk quantities.

Silver has been applied principally by electrolytic dissolution of the metal, principally in swimming pool applications. Incorporating silver in a filter medium, such as activated carbon, is an alternative approach. Silver is incorporated into granular activated carbon to prevent bacterial growth in the filter in home use applications.

Ultraviolet radiation can be applied to water in two distinctly different ways, each having advantages and disadvantages. Tubular reactors have the advantages of being sealed and under pressure but suffer the disadvantage of lamp fouling and the need for cleaning. The alternative approach is to place the lamps above the water surface, between the surface and a reflecting material. This approach is efficient, does not have a lamp fouling problem, but must operate under atmospheric pressure within an open vessel that can permit contamination. Problems that are common to both applications are adsorption of radiation by particulates as natural color, hydroxy radical scavengers, and the lack of a residual.

5.1.6 Summary

In summary, all of the above mentioned approaches may be now or potentially used to disinfect drinking water. The systems vary in cost, complexity, the hazard of the chemicals used, and the production of a disinfectant residual, but careful design and operation can produce satisfactory disinfection.

REFERENCES

1. J.J. Rook, Water Treatment and Examination, 23, 234 (Part 2, 1974).

2. T.A. Bellar, J.J. Lichtenberg, and R.C. Kroner, J. Am. Water Works Assoc. 66, 703 (1974).

3. J.M. Symons, T.A. Bellar, J.K. Carswell, J. DeMarco, K.L. Kropp, G.G. Robeck, D.R. Seeger, C.J. Slocum, B.L. Smith, and A.A. Stevens, J. Am. Water Works Assoc. 67, 634 (1975).

4. J. M. Symons, A.A. Stevens, R.M. Clark, E.E. Geldreich, O.T. Love, Jr., J. DeMarco, Treatment Techniques for Controlling Trihalomethanes in Drinking Water, American Water Works Association, Denver, 1982.

5. J.J. Rook, J. Am. Water Works Assoc. 68, 168 (1976).

6. W.W. Bunn, B.B. Haas, E.R. Deane, and R.D. Kleopfer, Environmental Letters, 10, 205 (1975).

7. A.A. Stevens, C.J. Slocum, D.R. Seeger and G.G. Robeck, J. Am. Water Works Assoc. 68, 615 (1976).

8. M. Kajino and M.Yagi, "Formation of Trihalomethanes During Chlorination and Determination of Halogenated Hydrocarbons in Drinking Water", In: B. K. Afghan and D. Mackay, Eds., Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment, Plenum, 1980, p. 491.

9. P.V. Scarpino, S. Cronier, M.L. Zink, F.A.O. Brigano, and J.C. Hoff, "Effect of Particulates on Disinfection of Enteroviruses and Coliform Bacteria in Water by Chlorine Dioxide". In Proceedings - Fifth Water Quality Technology Conference, Kansas City, MO, December 4-7, 1977, American Water Works Association, Devner, CO, 1978.

10. M.P. Esposito, "The Inactivation of Viruses in Water by Dichloramine", M.S. Thesis, University of Cincinnati, Cincinnati, OH, 1944.

11. R.S. Engelbrecht, M.J. Weber, B.B. Salter and C.A. Schmidt, Applied and Environmental Microbiology, 40, 249 (1980).

12. G.C. White, Handbook of Chlorination, Van Nostrand Reinhold, New York, NY, 1972.

13. M.A. Benarde, B.M. Israel, V.O. Olivieri and M.L. Granstrom, Applied Microbiology, 13, 776 (1965).

14. Safe Drinking Water Committee, Drinking Water and Health, Vol. 2, National Academy Press, Washington, DC, 1980.

15. J.C. Hoff, "The Relationship of Turbidity to Disinfection of Potable Water", In: C.H. Hendricks, Ed., Evaluation of the Microbiology Standards for Drinking Water, EPA-570/9-78-002, Washington, DC, 1978, NTIS Accession No. PB 297119.

16. T.W. Hijkal, F.M. Wellings, P.A. LaRock and A.L. Lewis, Applied and Environmental Microbiology, 35, 114 (1979).

17. A.T. Palin, Chemistry and Control of Modern Chlorination, 2nd ed., Lamotte Chemical Products, Chestertown, MD, 1983, p. 19.

18. R. P. Arber, M.A. Speed, F.Scully, "Significant Findings Related to the Formation of Chlorinated Organic Compounds in the Presence of Chloramines" presented at the Fifth Water Chlorination Conference; Environmental Impact and Health Effects, Williamsburg, VA, June 3-8, 1984.

19. A.A. Lange and E. Kawczynski, J. Am. Water Works Assoc., 70, 653 (1978).

20. C.A. Sorber, R.F. Williams, B.E. Moore, K.E. Longley, Alternative Water Disinfection Schemes for Reduced Trihalomethane Formation: Volume 1. Prototype Studies. EPA-600/S2-82-037, 1982.

21. R. Miltner, "The Effect of Chlorine Dioxide on Trihalomethanes in Drinking Water", M.S. Thesis, Unviversity of Cincinnati, Cincinnati, OH, 1976.

22. W.J. Copper, R.G. Zika, M.S. Steinhauer, "The Effect of Bromide in Water Treatment II. A Literature Review of Ozone and Bromide Interactions and the Formation of Organic Bromide", Presented at Meeting of International Ozone Assn. and National Institute for Water Research, Pretoria, South Africa, March 26-29, 1984.

23. J. Rickabaugh and R.N. Kinman, "Trihalomethane Formation from Iodine and Chlorine Disinfection of Ohio River Water", In: R.L. Jolley, H. Gorchev, and R.D. Hamilton Jr., Eds., Water Chlorination: Environmental Impact and Health Effects, Vol. II. Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1978, p. 583-591.

24. Federal Register, 44, No. 231, 68624-68707 (November 29, 1979); 45, 15542-15547 (March 11, 1980).

25. J.J. Rook, Environ. Sci. Technol., 11, 478 (1978).

26. L. Stieglitz, W. Roth, W. Kühn and W. Leger, Vom Wasser, 47, 347 (1976).

27. W.E. Coleman, R.D. Lingg, R.G. Melton, and F.C. Kopfler, "The Occurrence of Volatile Organics in Five Drinking Water Supplies Using Gas Chromatography/Mass Spectrometry", In: L. H. Keith, Ed., Identification and Analysis of Organic Pollutants in Water, Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1976, p. 305.

28. M.L. Trehy, T.I. Bieber, "Dihaloacetonitriles in Chlorinated Natural Waters" In: R. L. Jolley, et al., Eds., Water Chlorination: Environmental Impact and Health Effects, Vol. 4, Ann Arbor Science, Ann Arbor, MI, 1983, pp. 85-96.

29. I.H. Suffet, L. Brenner and B. Silver, Environ. Sci. Technol., 10, 1273 (1976).

30. R.F. Christman, D.L. Norwood, D.S. Millington, J.D. Johnson, A.A. Stevens, Environ. Sci. Technol., 17 625 (1983).

31. J.D. Johnson, R. F. Christman, D.L. Norwood and D.S. Millington, Environ. Health Perspectives, 46, 63 (1982).

32. D.L. Norwood, J.D. Johnson and R.F. Chrsistman, "Chlorinated Products from Aquatic Humic Material at Neutral pH", In: Robert L. Jolley et al. (eds), Water Chlorination: Environmental Impact and Health Effects, Vol. 4, Ann Arbor Science, Ann Arbor, MI, 1983.

33. D.R. Seeger, L.A. Moore, A.A. Stevens, "The Formation of Acidic Trace Organic Byproducts from the Chlorination of Humic Acids", Presented at the 5th Water Chlorination Conference: Environmental Impact and Health Effects, Williamsburg, VA, June 3-8, 1984.

34. A.P. Black and R.F. Christman, J. Am. Water Works Assoc. 55, 897 (1963).

35. A.A. Stevens. Environ. Health Perspectives, 46, 101 (1982).

36. C.A. Colclough, J.D. Johnson, D.S. Millington and R.F. Christman, "Organic Reaction Products of Chlorine Dioxide and Natural Aquatic Fulvic Acid", In: R. L. Jolley et al. eds, Water Chlorination: Environmental Impact and Health Effects, Vol. 4, Ann Arbor Science, Ann Arbor, MI, 1983.

37. M. Schalekamp, "Experience in Switzerland with Ozone, Particularly in Conncetion with the Neutralization of Hygenically Undersirable Elements Present in Water", In: Proceedings-1977 Annual Conference American Water Works Association, Anaheim, CA, May 8-13, 1977, American Water Works Association, Denver, CO, 1978.

38. R.E. Sievers, R.M. Barkley, G.A. Eiceman, R.H. Shapiro, H.F. Walton, K.J. Kolonko and L.R. Field, Journal of Chromatography, 142, 745 (1977).

39. U.S. EPA, Office of Drinking Water, Trihalomethanes in Drinking Water: Sampling, Analysis, Monitoring and Compliance, EPA 570/9-83-002, 1983, p. 31.

40. R.C. Dressman, B.A. Najar, R. Redzikowski. "The Analyses of Organohalides (OX) in Water as a Group Parameter". In: Proceedings 7th Annual AWWA Water Quality Technology Conference, American Water Works Assoc., Denver, CO, 1980, p. 69.

41. A.A. Stevens, L. Moore, R.C. Dressman, D.R. Seeger, "Disinfectant Chemsitry in Drinking Water - Overview of Impacts on Drinking Water Quality". Presented at 186th National Meeting, American Chemical Society, Washington, DC, 1983.

42. S.J. Fleischacker and S.J. Randke, J. Am. Water Works Assoc. 75, 132 (1983).

43. J.D. Johnson, Ed., Disinfection - Water and Wastewater, Ann Arbor Science, Ann Arbor, MI, 1975.

FIGURE CAPTIONS

Fig. 11. 1. Inactivation of E. coli (ATCC 11229) by free and combined chlorine species and chlorine dioxide (9, 10)

Fig. 11.2. Inactivation of poliovirus 1 (Mahoney) by free and combined chlorine species and chlorine dioxide (9, 10)

Fig. 11.3. Chlorine - ammonia breakpoint curve

Fig. 11.4. Chloroform formation by free and combined chlorine residual (4)

Fig. 11.5. Chloroform formation in water containing 5 mg/L humic acid dosed with chlorine-free chlorine dioxide or free chlorine (4)

Fig. 11.6. A comparison of the effects of pH and oxidant dose on the formation of NPOX and trihalomethanes ($CHCl_3$) at 20°C in distilled water solutions of 5 mg humic acid/L

Fig. 11.7. A comparison of the formation of NPOX and trihalomethanes ($CHCl_3$) at 20°C in distilled water solutions of 5 mg humic acid/L dosed with various disinfectants.

Fig 11.1

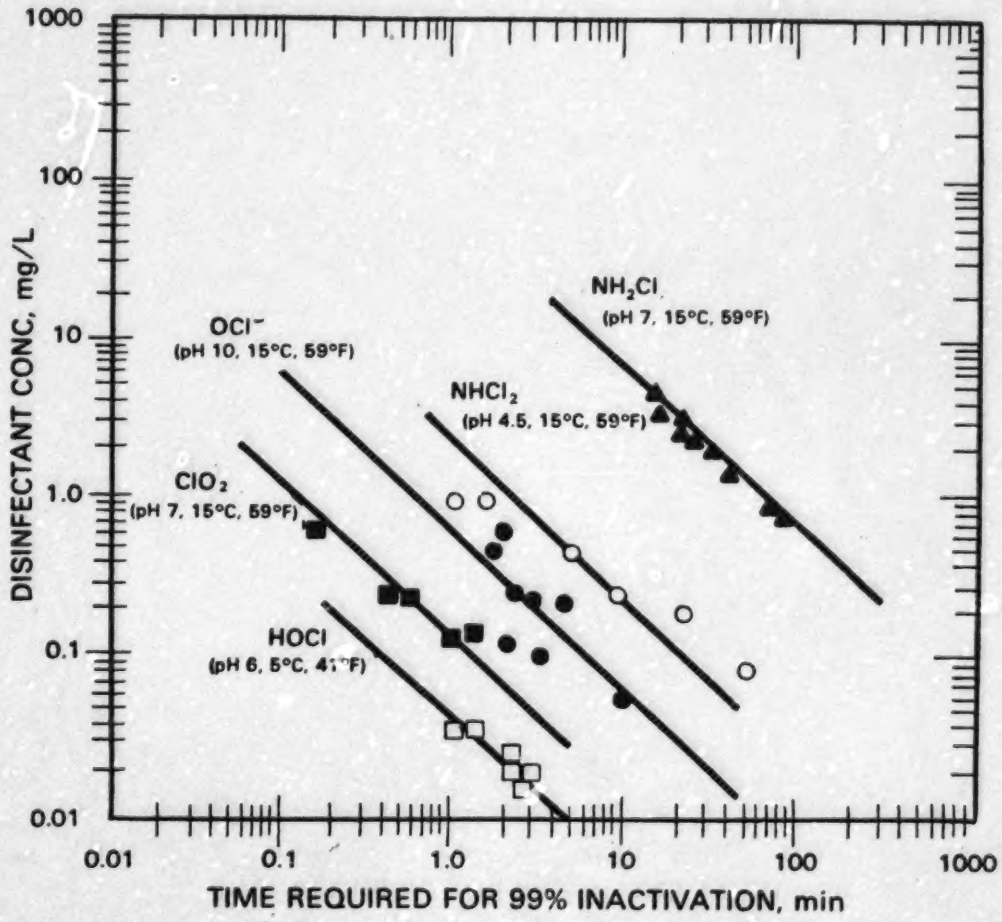
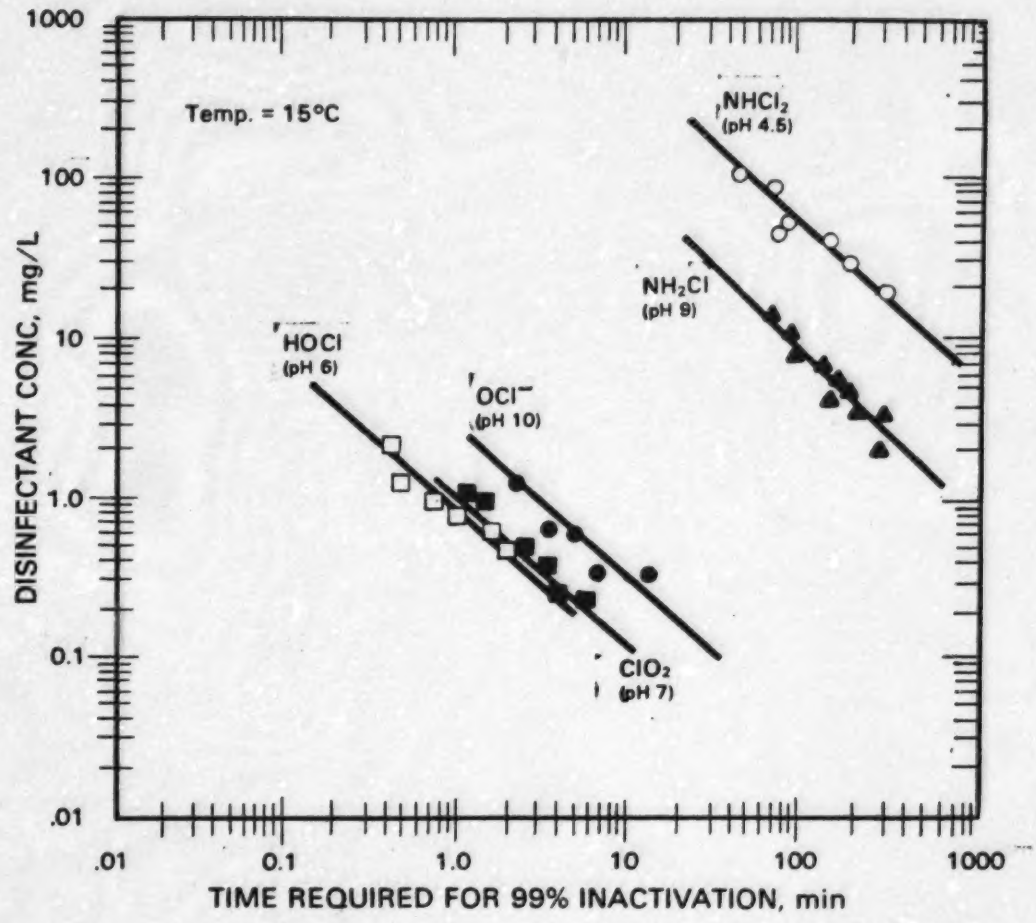
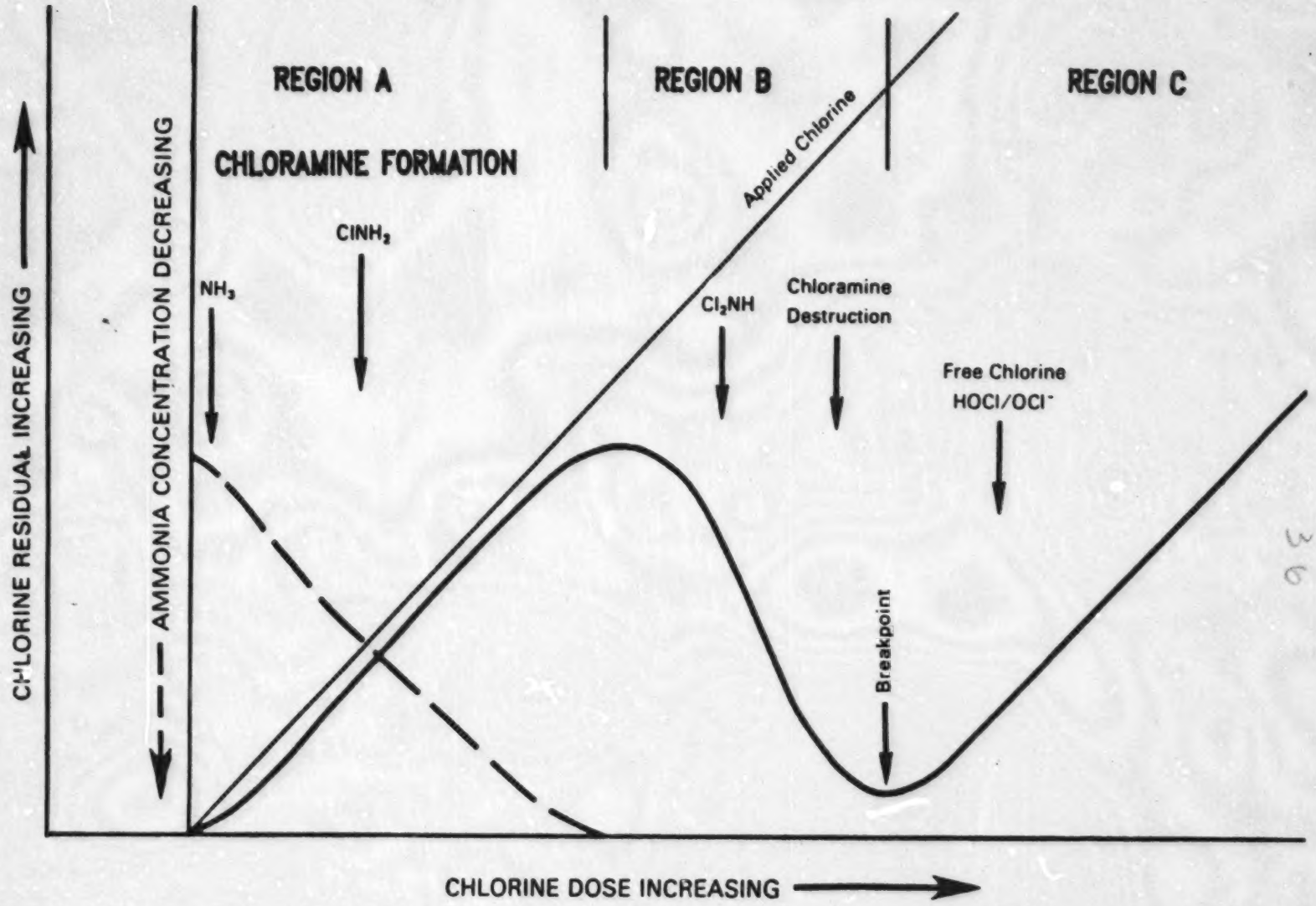

1000
100
10
1.0
0.1
0.01
DISINFECTANT CONC, mg/L
0.01
0.1
1.0
10
100
1000
TIME REQUIRED FOR 99% INACTIVATION, min
NH2Cl
(pH 7, 15°C, 59°F)
OCl⁻
(pH 10, 15°C, 59°F)
NHCl2
(pH 4.5, 15°C, 59°F)
ClO2
(pH 7, 15°C, 59°F)
HOCl
(pH 6, 5°C, 41°F)

Fig 11.2


Temp. = 15°C
NHCl2 (pH 4.5)
NH2Cl (pH 9)
HOCl (pH 6)
OCl⁻ (pH 10)
ClO2 (pH 7)
DISINFECTANT CONC, mg/L
1000
100
10
1.0
0.1
.01
.01
0.1
1.0
10
100
1000
TIME REQUIRED FOR 99% INACTIVATION, min


REGION A
CHLORAMINE FORMATION
REGION B
REGION C
Applied Chlorine
CINH2
NH3
Cl2NH
Chloramine
Destruction
Free Chlorine
HOCl/OCl-
Breakpoint
CHLORINE RESIDUAL INCREASING
AMMONIA CONCENTRATION DECREASING
CHLORINE DOSE INCREASING

36

Fig 11-2

Fig 11.4

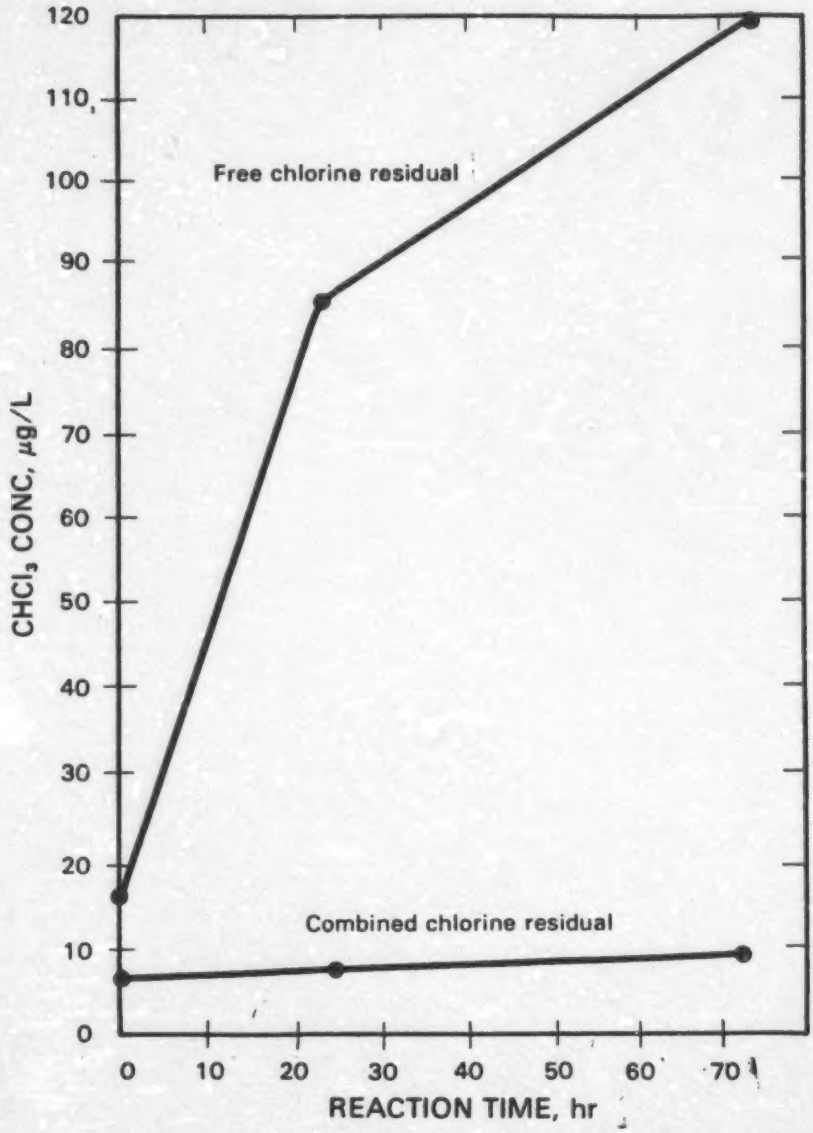

120
110
100
90
80
70
60
50
40
30
20
10
0
CHCl3 CONC, µg/L
Free chlorine residual
Combined chlorine residual
0
10
20
30
40
50
60
70
REACTION TIME, hr

Fig 11.5

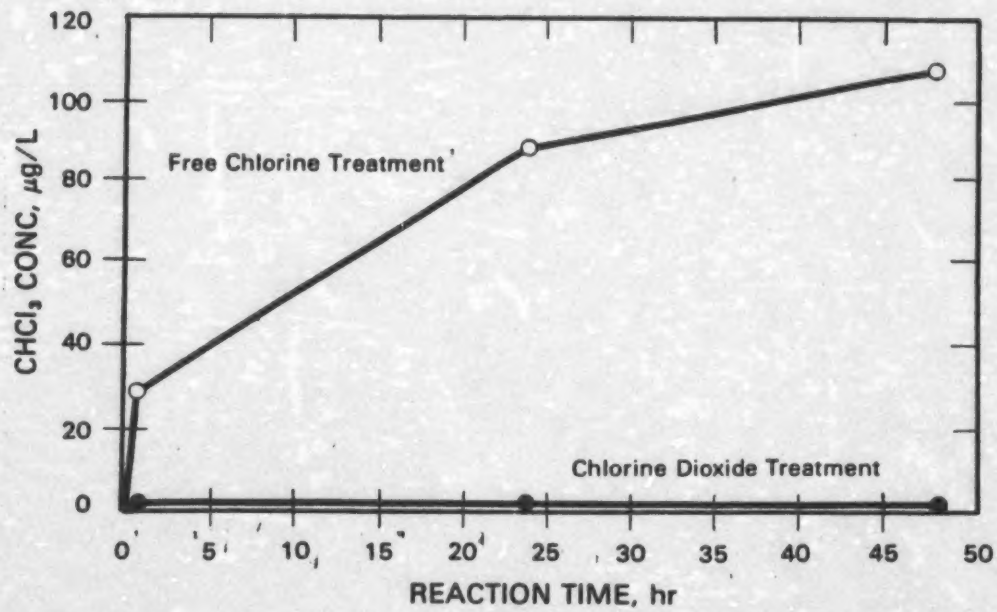

120
100
80
60
40
20
0
CHCl3 CONC, µg/L
Free Chlorine Treatment
Chlorine Dioxide Treatment
0
5
10
15
20
25
30
35
40
45
50
REACTION TIME, hr

Fig 4c

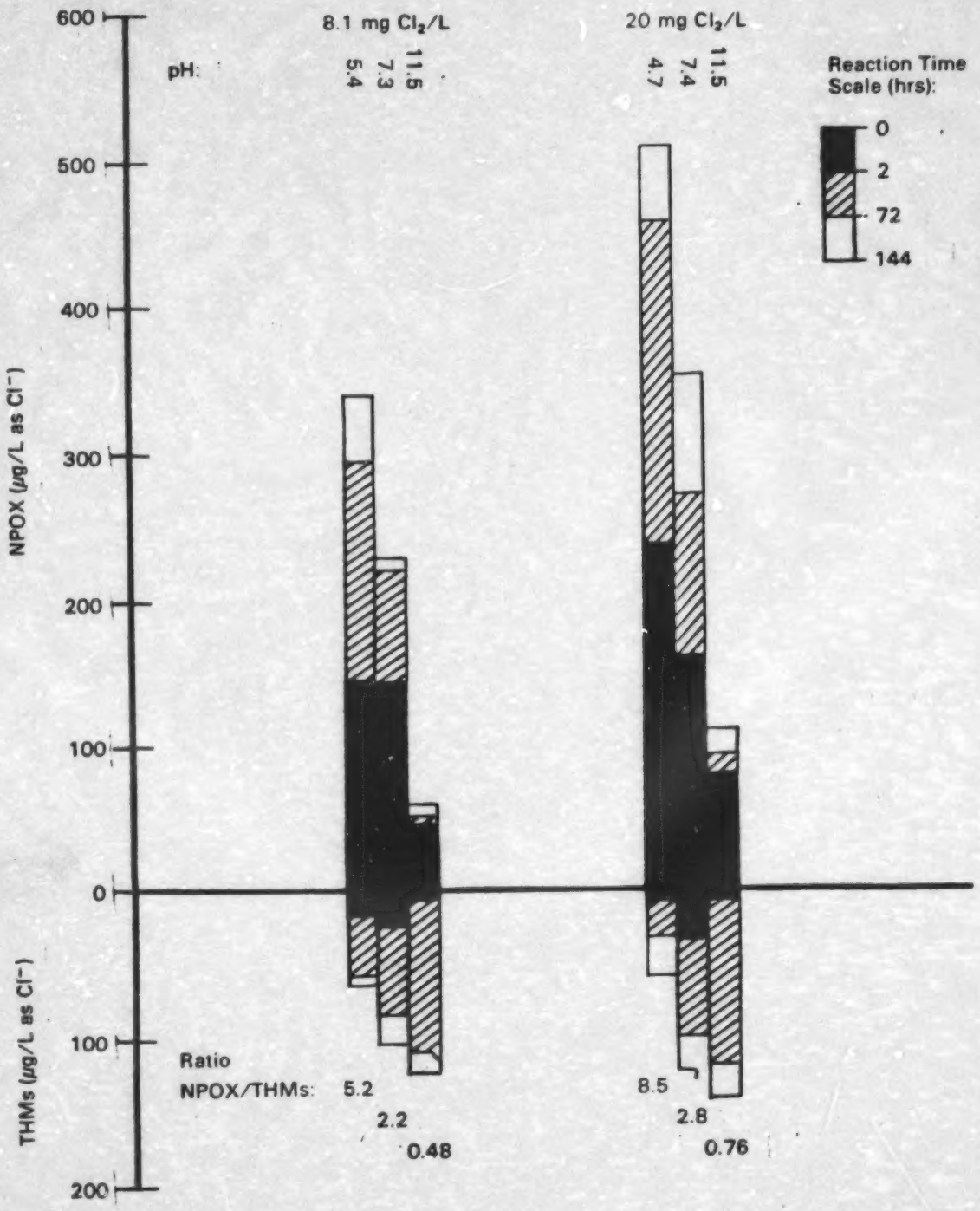
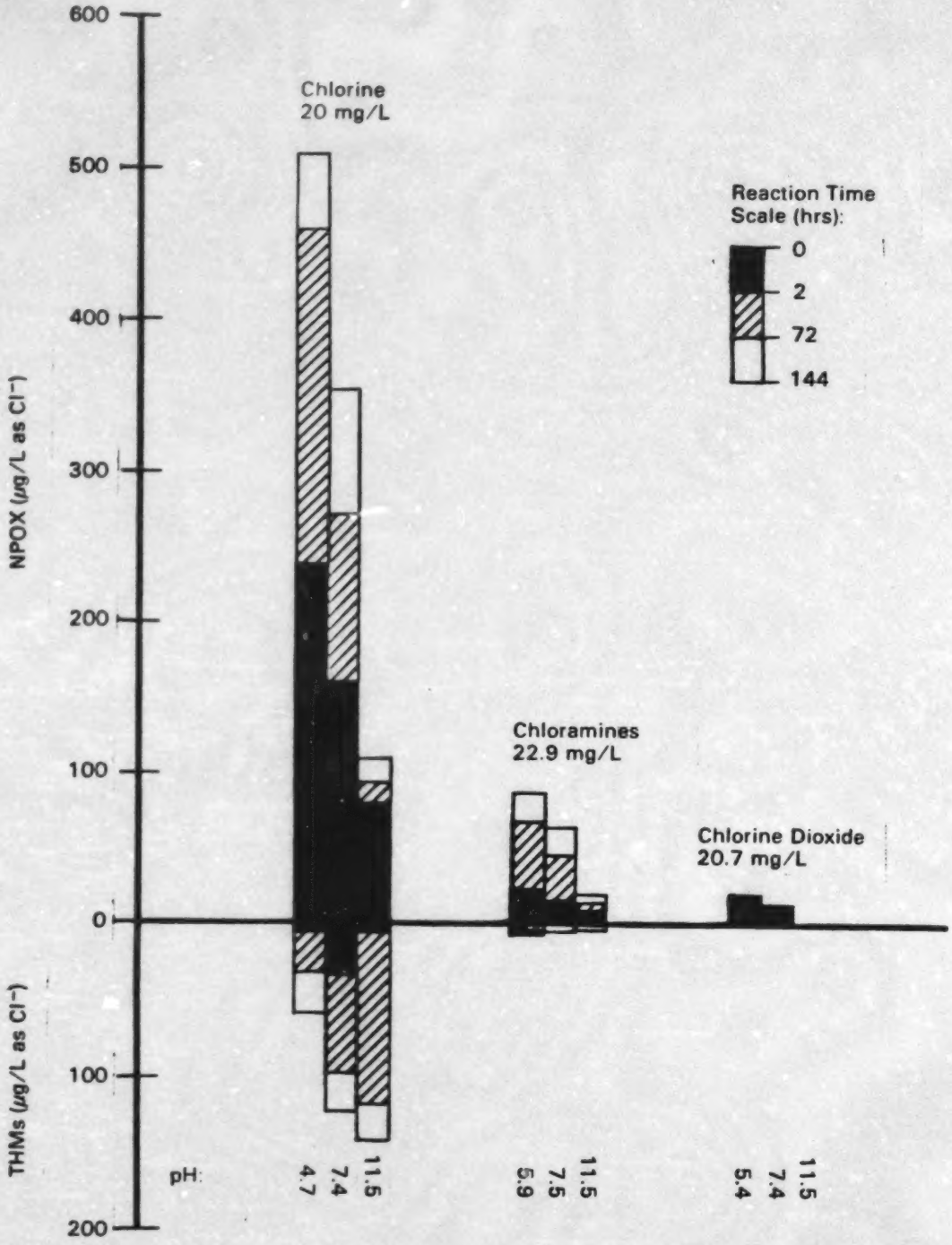

8.1 mg Cl2/L
20 mg Cl2/L
pH:
5.4
7.3
11.5
4.7
7.4
11.5
Reaction Time Scale (hrs):
0
2
72
144
600
500
400
300
200
100
0
100
200
NPOX (µg/L as Cl⁻)
THMs (µg/L as Cl⁻)
Ratio NPOX/THMs:
5.2
2.2
0.48
8.5
2.8
0.76

Fig 11.7


600
500
400
300
200
100
0
100
200
NPOX (μg/L as Cl⁻)
THMs (μg/L as Cl⁻)
Chlorine
20 mg/L
Chloramines
22.9 mg/L
Chlorine Dioxide
20.7 mg/L
Reaction Time
Scale (hrs):
0
2
72
144
pH:
4.7
7.4
11.5
5.9
7.5
11.5
5.4
7.4
11.5